7.   The isotherms, and isobars prepared from them, give effective evidence for the presence of two forms of adsorption, that occurring at the higher temperature requiring an activation energy.

8.   The heat of activated adsorption is calculated as 15,000 calories per mole on the less active portions of the surface.

9.   The determination of the effect of the change of temperature upon the amount of adsorption is shown to be a practical method for the investigation of the various forms of adsorption.

PRINCETON, NEW JERSEY

ON THE DISSOLUTION OF METALS IN ACIDS

BY J. N. BRÖNSTED AND N. L. ROSS KANE

1.   Introduction

The power of attacking and dissolving metals with evolution of hydrogen has from early times in the history of chemistry been considered as one of the most conspicuous and important characteristics of acids.   On this account a large number of investigations from various points of view have in the course of time been carried out.   The present paper contains an attempt to deal with the subject from the standpoint of the extended theory of acids and bases for which the reaction appears of particular significance.

By far the greater number of investigations on this reaction have dealt with impure or *heterogeneous* metals.   The effect of acids upon such materials has a great practical importance.   But the laws by which these reactions are governed are different from those of the simple reactions of homogeneous metals.   When intending to elucidate the kinetics of the reaction between acids and metals in its elementary form, the investigator is reduced to the use of pure or *homogeneous* material only.

The theory has been advanced by de la Rive[1] that the dissolution of ordinary metals in acids is an electrolytic reaction originating in the heterogeneity of the metal.   Palmaer[2] and his co-workers in extensive publications have brought convincing evidence in favor of this theory, which is known as the "theory of local elements."   As in the present paper the explanation of the mechanism is based upon the condition of homogeneity, it has not been necessary to deal with details as regards the theory of local elements.

[1] De la Rive, *Ann. chim. phys.*, **43**, 425 (1830).

[2] Erichson-Auren and Palmaer, *Z. physik. Chem.*, **39**, 1 (1901); **45**, 182 (1903); **56**, 689 (1906); Palmaer, *Ingeniörsvetenskaps-Akademiens Handlinger* (Stockholm), Nr. 93 (1929); *cf.* also Guertler and Blumenthal, *Z. physik. Chem.*, **152**, 197 (1931).

In the case of a homogeneous metal, the dissolution process may be looked upon as being a direct chemical reaction between the metal and the dissolved acid molecule at the interface of solution and metal. In the classical theory of electrolytic dissociation the hydrogen ion was generally considered as the unique carrier of acidity, and it appeared obvious to make this ion responsible also for the reaction between metals and acids. On this basis the observations on the influence of varying concentration of strong acids and the different behavior of strong and weak acids found at least a qualitative explanation. Failure to distinguish adequately between reactions with pure and impure metals, as well as several complications revealed in these reactions on closer examination, were factors that prevented an exact interpretation of the dissolving process as a mass action effect.

It has also been attempted from some quarters to explain the dissolution of metals as a diffusion process. Evidently the diffusion theory of heterogeneous reactions serves as a possible explanation only for reactions in which the chemical action is rapid compared with the diffusion process. There is no reason, however, to assume that the reaction of dissolved molecules with the molecules of a solid substance should be instantaneous or in any way more rapid than the reactions of dissolved molecules between themselves. The diffusion theory is therefore inapplicable for a general explanation of heterogeneous reactions. On the other hand, when the elementary reaction proceeds with sufficient rapidity, there is no doubt that the diffusion of the reacting acid to the interface plays a part more or less important for the dissolving process.[3]

A detailed discussion of the large amount of work done in the field of dissolution of metals in acids lies outside the scope of the present paper. For a complete literature list and discussion the reader is referred to Palmaer's monograph "The Corrosion of Metals," quoted above, and papers by Centnerszwer.[4] It should only be mentioned here that Kilpatrick and Rushton[5] have studied quite recently the dissolution of magnesium in various acids and buffers and have presented a clear verification of the points of view which are advocated in the present paper.

2. The Reaction Mechanism

We shall attempt to form a picture of the reaction mechanism on the basis of the following considerations. When a homogeneous metal reacts with an acid in an aqueous medium and goes into solution, the simplest mechanism would seem to be a reaction at the interface, e. g., as represented by the scheme

$$H^+ + Na \longrightarrow Na^+ + H \qquad (1)$$
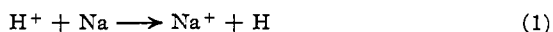
[3] Cf. Centnerszwer, Z. physik. Chem., 137, 352 (1928).

[4] Centnerszwer and Sachs, ibid., 87, 692 (1914); 89, 213 (1915) and other papers quoted below.

[5] Kilpatrick and Rushton. J. Phys. Chem., 34, 2180 (1930).

This apparently corresponds to the classical view in the theory of electrolytic dissociation. However, when we remember that the hydrogen ion in aqueous solution is H_3O^+ and, furthermore, that the metal in a solid state probably consists of metallic ions and free electrons, the scheme should be modified as follows

$$H_3O^+ + Na^+ + \ominus \longrightarrow H_2O + Na^+ + H \qquad (2)$$
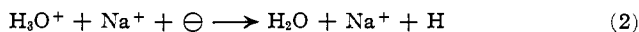
This reaction again can be divided into a "chemical" part

$$H_3O^+ + \ominus \longrightarrow H_2O + H$$

and a more "physical" part

$$\begin{matrix} Na^+ & \longrightarrow & Na^+ \\ \text{(solid)} & & \text{(dissolved)} \end{matrix} \qquad (3)$$
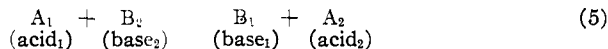
the latter being the actual dissolution process in which also hydration and similar actions may be effective.

According to the extended theory of acids and bases[6] H_3O^+ is an acid and H_2O the conjugate base. Neither of these is unique as regards acidity and basicity, and we must therefore conclude that in the above scheme they can be replaced by any pair of conjugate acids and bases. By such a substitution reaction (2) becomes generalized to

$$\begin{matrix} A & + \ominus \longrightarrow & B & + H \\ \text{(acid)} & & \text{(base)} \end{matrix} \qquad (4)$$
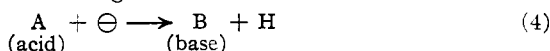
This is a special case of the still more general reaction between two pairs of conjugate acids and bases

$$\begin{matrix} A_1 & + & B_2 & & B_1 & + & A_2 \\ \text{(acid}_1) & & \text{(base}_2) & & \text{(base}_1) & & \text{(acid}_2) \end{matrix} \qquad (5)$$

fundamental to all protolytic reactions. It shows that the hydrogen atom is an acid to which the electron corresponds as the conjugate base.[7]
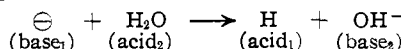
Obviously the above reactions only lead to the formation of hydrogen atoms. For hydrogen to escape in the gaseous state the atoms have to combine to form a molecule

$$2H \longrightarrow H_2 \qquad (6)$$

The kinetics of the total reaction therefore depends upon the way in which the three partial reactions (3), (4) and (6) are interrelated.

    [6] Brönsted, *Rec. trav. chim.*, **42**, 718 (1923); *J. Phys. Chem.*, **30**, 777 (1926); *Chem. Rev.*, **5**, 231 (1928); *Z. angew. Chem.*, **43**, 229 (1930).

    [7] The electron $\ominus$ takes the same position relative to metallic sodium as does the hydroxyl ion OH^- to sodium hydroxide. If NaOH is described as a base, the same description therefore applies to Na. It is, however, a much stronger base than NaOH. Therefore, when sodium dissolves in water, in which it is undoubtedly readily soluble, the protolytic reaction

$$\begin{matrix} \ominus & + & H_2O & \longrightarrow & H & + & OH^- \\ \text{(base}_1) & & \text{(acid}_2) & & \text{(acid}_1) & & \text{(base}_2) \end{matrix}$$

immediately takes place, masking the simple dissolution process. In ammonia, which is usually a poorer solvent toward electrolytes than water, sodium dissolves without giving rise to any such protolytic reaction, on account of the much weaker acid properties of NH_3 compared to H_2O, and consequently in this solvent a simple solution of metallic sodium is formed.

Since an electron is not tied up to any individual metallic ion in the metallic state, and since the condition of the contact between metal and solution when no acid is present undoubtedly is one of mobile equilibrium, an equal number of ions passing from the metal to the solution and the opposite way in a certain time, one may conclude that there is no strict stoichiometric relation between single elementary reactions of type (3) and (4). The effect of a single reaction (4) is only to increase the probability of a reaction (3) taking place, owing to the production of an electric potential or charge effect.

Reaction (3) therefore cannot be assumed to have any bearing upon the laws by which the total reaction is governed. They should be independent, for instance, of the valence of the metal going into solution.

Hence the equation for the total reaction depends upon reactions (4) and (6). Let us suppose that only the direct, and not the reversed reactions are effective. If H in scheme (6) means actually free hydrogen atoms in a normal state of energy, then, since these are not being accumulated, their formation must be slow compared to their combination to hydrogen molecules, and, disregarding "salt effects," the velocity of the hydrogen evolution should be a first order reaction as regards the concentration of the acid molecule A. On the other hand, it is possible that H_2 is formed also by the collision of the two hydrogen atoms only partly liberated from two A molecules, $i.\ e.$, by two hydrogen atoms at a low energy level. In that case the total reaction were more properly expressed as

$$2A + 2\ominus \longrightarrow 2B + H_2 \qquad (7)$$

and should be bimolecular as regards the A-concentration. According to the degree of liberty required for the union of the two hydrogen atoms, there might exist a transition between the two cases. Decreasing concentration of acid would then favor the first order reaction in relation to the second.

If reaction (6) is reversible, $i.\ e.$, if the hydrogen molecule at the metallic surface or in the body of the metal shows a detectable dissociation, this would not mean any change in the above conclusion.[8]

[8] It has been suggested [Tafel, $Z.\ physik.\ Chem.$, **34**, 187 (1900)] that the effect of the metallic surface upon the dissolving velocity and the overvoltage at the electrolytic hydrogen evolution depends upon the velocity with which the reaction $2H \longrightarrow H_2$ takes place. However, even if all collisions between hydrogen atoms were effective in forming molecules, the overvoltage with measurable current densities would not disappear. In the opinion of the present writers the overvoltage is determined by the activity coefficient of atomic hydrogen in the various metals. For a certain given concentration of hydrogen atoms the potential, for instance in platinum, is small, and the reaction $H^+ \longrightarrow H$ easily takes place. On the other hand, the potential of H in mercury is very large, and the corresponding reaction here proceeds much more difficultly. This is simply a question of the solubility of atomic hydrogen in the different metals. It makes no difference to these results whether the hydrogen atoms are supposed to dissociate into protons and electrons in the metal or not.

It has also been suggested that the forces opposing the formation of very small

If reaction (4) is also a reversible reaction

$$A + \ominus \rightleftharpoons B + H$$
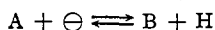
and (6) is slow compared to both of these, then at constant c_B the concentration of H would be proportional to c_A and the velocity of the H_2-formation proportional to $c_A{}^2$. In this case the total reaction would be a second order reaction as regards the acid concentration.

It is not possible with certainty to predict which of the above cases applies to the reaction. The experiments, however, agree fairly well with the assumption of a first order reaction as regards the effect of the acid. On the basis of the above considerations we have therefore concluded that the mechanism of the kinetic reaction is represented by scheme (4)

$$A + \ominus \longrightarrow B + H$$
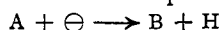
the hydrogen atoms being liberated in the normal state and thereafter reacting with great velocity to form hydrogen molecules. Whether the last mentioned reaction is simple or complex[9] is insignificant if only it is rapid compared to (4).

In the above scheme A may be the hydrion H_3O^-, but, in accordance with the extended theory of acids, it may be just as well another acid molecule.

It should be added, that even if this point of view seems well applicable to the simple reaction between metals and acids in dilute solution, there is another mechanism of reaction, which cannot be excluded as a primary cause of this process in certain cases. Just as the primary union of the proton from the acid molecule with the electron from the metal is followed by the passage of metallic ions from the metal into the solution, it is possible that an electric combination of the metallic ion in the solid state with an anion from the solution may be the primary cause for an electron to combine with a proton. Such a reaction between the metallic ion and an anion, which might be a simple electric union or might be the transient formation of a true chemical compound, is however not so probable as the primary reaction of the proton. It should be the more probable the higher the valence of the metal going into solution. The results of Centnerszwer[10,11] corroborate this view. The calculations made by this author in support of the idea of a reaction between the metal and undissociated acid and the attempts to determine the order of reaction in a number of cases are, however, not acceptable since they rest upon the applications of conductivity as a measure of dissociation and of the applicability of the mass action law

bubbles might be effective in producing overvoltage and retardation in the dissolution of metals. This is undoubtedly a quite inapplicable explanation, since the hydrogen is formed primarily in the dissolved state.

[9] *Cf.* Erdey-Gruz and Volmer, *Z. physik. Chem.*, 150, 203 (1930), where the question of overvoltage is discussed.

[10] Centnerszwer and Zablockie, *ibid.*, **122**, 455 (1926).

[11] Centnerszwer, *ibid.*, **141**, 297 (1929).

to electrolytes at very high concentrations, thus entirely disregarding the results of the more recent development of the theory of electrolytic dissociation.

3. The Decomposition of Sodium Amalgam

The process studied in the present investigation was the dissolution of sodium from sodium amalgam. This reaction was chosen because it is more easy to avoid, or at least to eliminate sufficiently, the errors due to impurities if the metal employed is present in the liquid state.

The decomposition of sodium amalgam in aqueous solutions has been studied by Klein,[12] Fraenckel and Heinz,[13] and Fraenckel, Wengel and Cahn.[14] All these investigators used concentrated amalgams containing about 0.50% sodium by weight, i. e., approximately 3.0 molar in sodium. The aqueous solutions employed contained sodium chloride, and sodium chloride with varying amounts of hydrochloric acid. Klein used quantities of amalgam large compared with the amount being decomposed, so that during an experiment the concentration of sodium in the amalgam could be considered constant. On the other hand, the other workers used quantities of solution whose sodium chloride and hydrochloric acid concentrations were many times in excess of those corresponding to the amount of sodium in the amalgam.

Klein was unable to reproduce his results in alkaline solution, but in acid solution he met with more success and showed that the velocity of reaction could be considered as made up of two terms, one corresponding to the velocity in neutral and weakly alkaline solutions, and the other proportional to the concentration of the acid.

Fraenckel and Heinz used acid solutions and found that the reaction proceeded with constant velocity until just before the end, when the rate suddenly fell practically to zero as the last traces of sodium were dissolved. Their assumption of the existence of a compound of sodium and mercury is not sufficient to account for this peculiarity.

In a later paper Fraenckel, Wengel and Cahn found that after the constant velocity period the reaction appeared to be unimolecular after the sodium concentration had fallen to between 0.5 and 1.0 milliequivalent per 100 g. of mercury. This conclusion is based on three experiments only, whose unimolecular constants differed considerably; moreover, in the one experiment whose data are given in detail the constants show a decided drift and vary by 10%, so that the evidence in favor of a unimolecular reaction is unconvincing.

In the present work the initial concentration of amalgam was much smaller than those above, and the changes in the acidic character of the solu-

[12] Klein, *Z. anorg. Chem.*, **137**, 39 (1924).

[13] Fraenckel and Heinz, *ibid.*, **133**, 153 (1924).

[14] Fraenckel, Wengel and Cahn, *ibid.*, **171**, 82 (1928).

tion were therefore in most cases insignificant. It was usual to employ 21.0 cc. of an amalgam which was 0.024 molal in sodium, $i.\ e.$, 0.19 milliequivalent of sodium per 100 g. mercury, less than the concentration at which Fraenckel, Wengel and Cahn found a unimolecular reaction to begin. No indication of a unimolecular reaction has ever been found in these experiments. About P_H 7.5 was the higher limit of acidity which could be used; with more acid solutions the reaction proceeded too quickly to admit of accurate measurements. Also, the mechanism of the chemical reaction is more likely to be masked by the diffusion process when the reaction is rapid. In the first series of experiments, which were mainly concerned with reproducibility, the influence of the initial amalgam concentration, and the effect of shaking, solutions of 2.0 molal K_2HPO_4 were used. The effect of the hydrogen ion in this solution is quite small and it shows a definite behavior toward amalgam although it has only a small buffer effect. In the second series the reaction in sodium hydroxide solution was studied in some detail. In the third various buffer mixtures were used and the catalytic properties of the acid molecules and ions contained in them investigated. Finally, some experiments were performed in benzene solution and the catalytic effect of phenol was measured over a range of concentrations.

4.   Experimental Procedure

The amalgam was prepared according to the method of Richards and Conant[15] in which a saturated solution of sodium carbonate is electrolyzed with a mercury cathode and a platinum anode. The mercury was first chemically purified by anodic treatment with an electric current using a dilute solution of nitric acid as electrolyte, and afterward thrice distilled. The amalgam was diluted to a suitable concentration and dried by gentle agitation $in\ vacuo$. Until ready for use it was kept $in\ vacuo$, and then sucked through a long capillary into the amalgam reservoir, which was previously completely evacuated. The capillary thereafter was sealed. In this way 500 cc. of a clean bright product was obtained indistinguishable from mercury, and remaining unchanged during the whole investigation, $i.\ e.$, about ten months.

The apparatus used is shown in Fig. 1. It consists of a reaction flask C communicating with the amalgam reservoir A through a thin flexible capillary and with the manometer and pump through the somewhat wider but similarly flexible capillary D. By turning the tap J_1 amalgam could be run into the buret B, and therefrom by turning tap T_2 a measured amount of amalgam could be run into the reaction flask, which contained already pure mercury and the solution. It was usual to take 0.50 cc. of the 1-molal stock amalgam diluted with 20.5 cc. of mercury ($i.\ e.$, 21 cc. of 0.024 molal amalgam) in each experiment and the following procedure was adapted. The reaction flask C was first cleared and dried by evacuating it through the right-hand capillary. The 20.5 cc. of mercury was then added through a funnel with a capillary stem and the solution under examination poured on top of the mercury. With non-aqueous solutions the procedure was modified slightly, thus: the solution was made up in a flask to which a tube could be fitted leading into the reaction flask C, which had previously been carefully dried and filled with dry air. By slightly evacuating C through the right-hand

[15] Richards and Conant, THIS JOURNAL, 44, 601 (1922).

capillary the solution could be sucked over without coming into contact with anything but dry air.

The stopper was then placed in position and the whole system evacuated through F for about two minutes. This always caused a small amount of amalgam remaining in the left-hand capillary to run into the flask, and this amount was always allowed to react sufficiently before the main experiment was begun. Then the flask was evacuated for about five minutes while being shaken all the time. When no more bubbles were seen to form on the mercury surface (shaking being momentarily stopped), the tap E communicating with the manometer was opened and the zero reading obtained. About fifteen minutes were allowed to elapse to make sure that this reading was steady, after which the reaction was begun by opening T_2 and running in 0.50 cc. of amalgam from the buret B. Readings of the manometer were taken in the usual way, both limbs b.ing
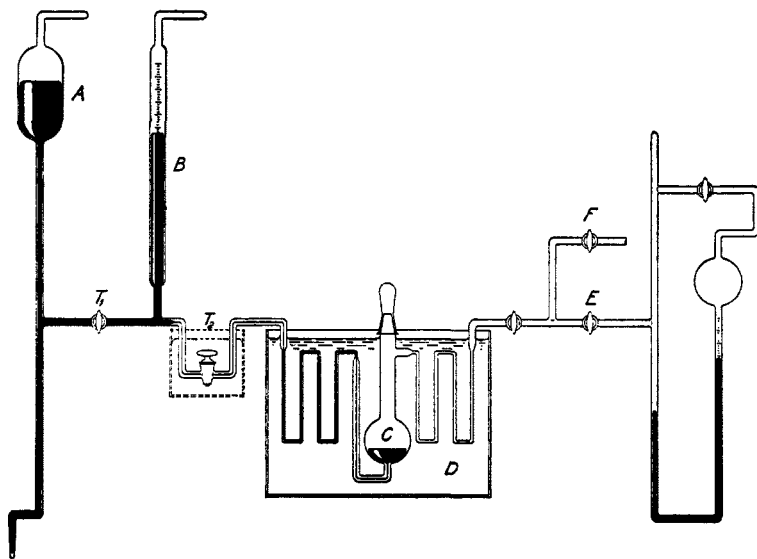

Fig. 1.

read. The reaction was considered complete when the manometer reading was seen to have reached a constant value and no bubbles were seen to form on the mercury surface. There was never any doubt about this final value, and the suddenness with which the reactions stopped is most striking; thus at a certain time near the end-point it would be noticed that the pressure increase was falling off rapidly, after a few minutes more the reaction would stop completely, and the mercury surface remain clear indefinitely. Fraenckel and Heinz also noted the sudden stopping in their experiments with strong acids.

The total pressure increase in our experiments using 0.5 cc. of the 1 molal stock amalgam was about 30 mm. The temperature was in all cases 18 $\pm$ 0.02°.

5. Effect of Amalgam Concentration

When pressure readings were plotted against times, the curves obtained were not those of unimolecular reactions; moreover, the sudden stopping of the reaction is not compatible with unimolecular processes. On ex-

amination, however, an approximately linear relation was found to exist between the velocity and the square root of the concentration of sodium in the amalgam.

This relationship is expressed by

$$-\frac{dx}{dt} = k\sqrt{x} \tag{8}$$

or

$$k = -2\frac{d\sqrt{x}}{dt} \tag{9}$$

where x is the concentration of sodium in the amalgam. On integration

$$kt = 2(\sqrt{a} - \sqrt{x}) \tag{10}$$

where a is initial sodium concentration. Obviously according to these equations a straight line should be obtained by plotting times against the square root of the sodium concentrations. Moreover, in a given solution the slope of this line (*i. e.*, $-k/2$) should be independent of the initial concentration of the sodium.

For a given solution the concentration of sodium at any time t is proportional to $p_\infty - p$, where p_∞ is final pressure increase and p is increase after time t, and so one can just as well plot $\sqrt{p_\infty - p}$ against t in order to test the relation; or, what amounts to the same thing, one can express the sodium concentration in terms of hydrogen pressure. The value of k in all calculations is obtained by putting the pressure of 1 cm. of mercury equal to unit sodium concentration, and using for t the time in minutes.

Thus if $p_\infty = 4$ cm. and after ten minutes $p = 3$ cm., then the reaction constant is $k = 0.2$.

The values of k, which we shall call the velocity constant of the reaction, depend upon the dimensions of the apparatus and are only directly comparable when these are kept constant, as in our experiments. They also vary slightly with the solution employed due to the changing solubility of hydrogen therein, but these variations are negligible.

TABLE I

EXPERIMENTAL DATA

Solution	Initial Na concn. in arbitrary units	$k \cdot 10^2$
2.0 molar K_2HPO_4	2	5.33
2.0 molar K_2HPO_4	4	5.20
2.0 molar K_2HPO_4	8	5.20
	Average	5.24
"9/1 Glycocoll" buffer	1	6.06
"9/1 Glycocoll" buffer	2	6.26
"9/1 Glycocoll" buffer	4	6.06
"9/1 Glycocoll" buffer	8	6.00
	Average	6.10

These deductions were tested first in solutions of 2.0 molal K_2HPO_4 and afterward in buffer mixtures of sodium glycocollate/glycocoll and ample verification obtained. In the K_2HPO_4 experiments the initial sodium concentration was varied in the ratio 1 to 4, while in the glycocoll buffer experiments it was varied from 1 to 8. In each solution a series of parallel lines was obtained from the slope of which the reaction constant was determined.

These figures show that the k-values are independent of the sodium concentration.

With the exception of sodium hydroxide solutions the experiments in aqueous solution were always reproducible. For example, in six identical experiments in which solutions of 2.0 molal K_2HPO_4 were used, the following values of k were obtained

$k \cdot 10^2$.................   5.30   5.46   5.33   5.26   5.46   5.40

This linear relation between time and sodium concentration holds good in all the solutions examined, both aqueous and non-aqueous, with the exception of solutions of benzoic acid in dry benzene, where possibly a chemical effect may have occurred. Toward the end of the experiments there is sometimes a drift away from linearity, but this is most likely to be due to the small changes in p and the corresponding uncertainty of the values $p_\infty - p$.

While the kinetic equation of a unimolecular reaction and a reaction of a higher order requires an infinitely long time for the reaction to be completed, the reaction described above for the dissolution of sodium amalgam is interesting in the fact that the time necessary for completion is finite. When in the equation

$$kt = 2(\sqrt{a} - \sqrt{x})$$

we insert $x = 0$ and the corresponding time t_∞ by which the reaction is completed we get

$$t_\infty = \frac{2\sqrt{a}}{k} \tag{11}$$

This is the *reaction time*. The relation is a special case of a more general equation

$$kt = \frac{a^{1-n} - x^{1-n}}{1 - n} \tag{12}$$

valid for a reaction of the n'th order. This obviously gives a finite t, *i. e.*, a finite reaction time for all values of n less than unity.

The existence of such a simple relation representing the velocity in practically all cases examined in this work is of great assistance in the interpretation of the results. There is no doubt that the k-values as calculated above can be taken as a measure of the kinetic activity of the solution regardless of the amalgam concentration.

Since a in all our experiments was about three, the reaction time according to equation (10) is determined by

$$kt_\infty = 3.5 \tag{13}$$

Thus it is easy from the reaction constants of the different acids to determine the time necessary for the reaction to become completed.

6.   The Influence of Shaking Speed

If the amalgam was not shaken the evolution of gas bubbles preferably concentrated at one point near the middle of the surface.   There are two explanations of this phenomenon.   One is that reaction does indeed only take place there, owing to some local impurity possessing a small overvoltage compared to the amalgam surface.   The process would then be electrolytic in nature and in conformity with the local element theory. The other explanation is that reaction does take place equally all over the surface, but that the surface forces attract all the hardly visible bubbles toward the center, where they unite and leave the surface.   Such a tendency exists at least for visible bubbles, as these often have been seen traveling toward the center as along the spokes of a wheel.   Moreover, if a trace of local impurity were responsible, then the results would not be reproducible.   Of course in all actual experiments the amalgam was always vigorously shaken and it was impossible to observe in what way the bubbles were formed.

The shaking speed was electrically controlled by a centrifugal governor and the variations in the rotation velocity did not exceed 1%.

With the apparatus used it was not possible to shake amalgam and solution separately, nor was it possible to shake the amalgam without altering its surface area.   Moreover, there was always a certain amount of reaction taking place at the areas of contact of amalgam and glass owing to the film of solution imprisoned there.   The more violent the shaking the larger this film.

Apart from these experiments in which the influence of shaking speed was under examination, the rotation of the regulator was always maintained at a constant speed.

A series of experiments in 2.0 molal K_2HPO_4 with different shaking speed showed the results in Table II.

<div align="center">

TABLE II

RESULTS OF EXPERIMENTS

</div>

Number of shakings per min...............	126	144	149	161
$k \cdot 10^2$...................................	4.46	5.86	6.26	7.80

The change from 126 to 161 means a very considerable alteration in the way in which amalgam and solution are brought in contact.   Obviously the slower the shaking the slower the reaction.

On the other hand, in the experiments in a glycocoll buffer solution the speed of the reaction was practically constant. With solutions of sodium hydroxide the results were not reproducible and the effect of shaking could not be determined.

7. Experiments with Sodium Hydroxide Solutions

The most remarkable result obtained with solutions of sodium hydroxide is the lack of reproducibility. Table III gives the figures for a number of experiments in sodium hydroxide solutions.

TABLE III

RESULTS OF EXPERIMENTS IN SODIUM HYDROXIDE SOLUTION

Date	Molality of NaOH	$k \cdot 10^2$
1–15–30	0.00	0.15
1–14–30	.01	.44
1–13–30	.10	.02
1–25–30	.10	.04
1– 9–30	.20	.08
1–20–30	.50	.50
12–13–29	.50	.48
1–18–30	.50	.16
1–10–30	.50	.12
1–16–30	1.00	.10
1–11–30	1.00	.04

In investigating the lack of reproducibility the following experiments were carried out: (a) a series using alternately 0.5 molar sodium hydroxide and 2.0 molar K_2HPO_4, with the results given in Table IV, showing that it was always possible to obtain the same quick reaction with 2.0 molar K_2HPO_4 regardless of the result of the intermediate sodium hydroxide experiment.

TABLE IV

APPROXIMATE VALUES OF k IN EXPT. (a)

Solution	$k \cdot 10^2$
2.0 M K_2HPO_4	5.33
0.50 M NaOH	0.16
2.0 M K_2HPO_4	5.32
0.50 M NaOH	0.50
2.0 M K_2HPO_4	5.33
0.50 M NaOH ·	0.20

(b) A series in which the solution ($N/10$ NaOH) was not renewed, while several successive portions of amalgam were added. These results would have been expected to be reproducible, but they were definitely not so, the values of $k \cdot 10^2$ in four experiments being 0.25, 0.45, 0.44 and 0.28.

(c) A series in which the mercury was not renewed while successive portions of amalgam were added; the solution meanwhile alternating

between 0.10 molar sodium hydroxide and 2.0 molar K_2HPO_4.   This series would be expected to show whether the lack of reproducibility was due to some conducting material left behind in the mercury surface, but the results did not support this supposition.

8.   Experiments in Phosphate Buffers

A buffer solution was made up containing 0.35 molar Na_2HPO_4, 0.15 molar NaH_2PO_4, 0.118 molar Na_2SO_4 and a series of experiments made with it, and with the solutions obtained by diluting it with a solution containing 0.468 molar Na_2SO_4 and 0.15 molar NaCl, the ionic strength and type thus being kept constant.   The reaction took place rather rapidly and it was found that there was a linear relation between the velocity constant and the concentration of the buffer, showing the presence of an acid effect different from the effect of the hydrogen ion.

TABLE V

EXPERIMENTAL DATA

Molality of NaH_2PO_4	Molality of Na_2HPO_4	$k \cdot 10^3$
0.015	0.035	16
.045	.105	27
.075	.175	36
.112	.261	45
.15	.35	57.5

9.   Experiments in Glycocoll Buffers

The buffer solutions were made by mixing a solution containing glycocoll and sodium chloride both at a concentration of 1.0 molar with varying amounts of 1.0 molar sodium hydroxide, thus keeping the ionic strength and type constant.   Three such buffers were used, with the compositions by volume given in Table VI.

TABLE VI

COMPOSITION OF GLYCOCOLL BUFFERS

r	m_{Gl}	m_{Gl^-}	R	P_H
9/1	0.8	0.1	8/1	8.9
7/3	.4	.3	3/4	9.7
6/4	.2	.4	2/4	10.1

r is the ratio of volumes glycocoll/glycocollate solutions, m the molalities, R the ratio m_{Gl}/m_{Gl^-} in the solution and P_H the approximate hydrogen exponent.   In these strong solutions this is known, however, only with a rough approximation.

With each buffer a series of experiments was carried out first with the buffer alone and then with the solutions obtained by diluting it with a solution of molar sodium chloride.   In this way it is possible to examine the catalytic effect of the glycocoll molecule over a range of concentrations and at three different P_H values.

TABLE VII

EXPERIMENTAL DATA

| Buffer	Molality of glyeocoll	Molality of glycocollate	$k \cdot 10^{3}$
9/1	0.08	0.010	1.33
9/1	.12	.015	2.06
9/1	.20	.025	2.60
9/1	.28	.035	3.10
9/1	.40	.050	3.86
9/1	.52	.065	4.90
9/1	.60	.075	4.93
9/1	.68	.085	5.96
9/1	.80	.100	6.40
7/3	.08	.060	1.13
7/3	.14	.105	1.43
7/3	.20	.150	1.83
7/3	.30	.225	2.50
7/3	.40	.300	3.13
6/4	.10	.20	1.20
6/4	.15	.30	1.33
6/4	.20	.40	1.96

The results show that there is a linear relation between the velocity constant and the glycocoll concentration in all three buffers and further that the three lines thus obtained are parallel. This conforms with the assumption of catalysis by the glycocoll molecule.

Further, the results reveal that the effect of the hydrogen ion in these experiments is comparatively small. Thus although the hydrion concentration is changed some sixteen-fold in passing from the 9/1 to the 6/4 buffers, the value of k is only about halved.

In order to try whether in the reaction studied a conductivity effect might be present to some extent, some experiments were carried out with glycocoll buffers in the presence of a varied amount of sodium chloride. If the evolution of hydrogen from the amalgam surface was due in part to an electrolytic cell being set up between the amalgam and a trace of conducting material of low overvoltage, the conductivity of the solution would be expected to have some effect on the reaction velocity as in many cases of dissolution of heterogeneous metals. The solutions employed were 7/3-glycocoll buffers containing various amounts of sodium chloride. One would expect an increase in velocity with increasing sodium chloride concentration if the conductivity effect was of appreciable size, provided that the salt effect of the added sodium chloride was negligible. The results showed that the greater the sodium chloride concentration the smaller is the reaction velocity. It is therefore improbable that there is any conductivity effect in the action of these buffers on sodium amalgam.

In order further to test the idea of a reaction mechanism in which the various acid molecules are directly effective, the influence of an addition of

the aquo-pentammine cobaltic or roseo ion was studied. The roseo ion dissociates in aqueous solution according to the scheme

$$\left[Co_{(NH_3)_5}^{H_2O}\right]^{+++} + H_2O \longrightarrow \left[Co_{(NH_3)_5}^{OH}\right]^{++} + H_3O^+$$
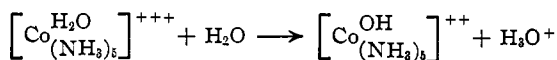
Due to the high positive charge of the acid one should expect it to react with particular readiness.

At first the roseo perchlorate was added at a concentration of 0.01 mole to the 7/3-glycocoll buffer diluted with its own volume of molal sodium chloride. The result obtained was a very sudden reaction, very short and violent but with an evolution of only about 10% of the usual amount of hydrogen. The reaction was over in less than one minute and in that time all the amalgam must have been used up, because the addition of hydro-chloric acid to the mercury in the reaction flask produced no gas evolution afterward. The solution was still pink after the reaction. The experiment was repeated three times, each time with the same result. Next the experiment was repeated with the roseo perchlorate at 0.001 molar and in this case there was a very fast reaction evolving about 50% of the usual amount of hydrogen. The pink color due to the roseo ion gradually faded as the reaction proceeded, but it was still noticeable at the end-point. Finally, the perchlorate was added at 0.0001 and in this case about the usual amount of hydrogen was evolved and the pink color entirely dis-appeared. The speed of the reaction was appreciably greater than that with the buffer alone.

There seems no doubt that the sodium amalgam reacts with the roseo perchlorate, but at the same time there is ample indication that the roseo ion has a large dissolving effect.

Even if the disappearance of the color of the roseo ion indicates that the ion is gradually reduced, the strong increase in reaction velocity on addition of the roseo salt leaves no doubt that the reaction between amalgam and roseo ion is a very rapid one. As the stoichiometric proportion of the roseo ion to the constituents of the buffer was very small, it is justifiable to look upon this phenomenon as a case of acid catalysis.

One might suggest that the high velocity was possibly produced by reduction of the salt and separation of metallic cobalt on the surface of the amalgam. However, when sodium amalgam was added after com-pletion of the reaction, the ordinary slow reaction of the glycocoll buffer was observed, which is incompatible with the assumption of a metallic catalyst as a cause of the velocity.

10. Experiments in Phenol Buffers

Phenol has a dissociation constant of about 10^{-10} at 18° and so a buffer containing 0.5 molar phenol and 0.25 molar sodium phenate should be of a suitable acidity. Such a buffer was made by taking a molal solution of

phenol in molal sodium chloride and mixing it with one-third of this volume of molal sodium hydroxide.

A series of experiments was carried out as in the case of the glycocoll buffer, the dilutions being effected with molal sodium chloride.

The results show just as in the glycocoll case an effect which varies linearly with the buffer concentration.

TABLE VIII

EXPERIMENTAL DATA

Molality of phenol	Molality of sodium phenate	$k \cdot 10^2$
0.05	0.0250	0.216
.115	.0575	.255
.250	.125	.311
.375	.188	.361
.50	.25	.422

11.   Experiments in Non-Aqueous Solutions

Zecchini[16] has compared the rates with which zinc dissolves in hydrochloric acid in various solvents and found that the velocity in the following series: ether, acetone, methyl alcohol, ethyl alcohol, water, amyl alcohol decreases from ether to amyl alcohol.

It appears from this sequence that the degree of dissociation is by no means the only factor determining the rate of reaction.   It is probable that the reaction occurs at least in part with the molecule of the undissociated hydrochloric acid; but other factors than the concentration of that acid molecule are obviously of importance.

In order to bring some further evidence for the reactivity of acids, in general, in the dissolution of metals, we have made a few experiments with sodium amalgam using benzene as a solvent.   In such an *aprotic* medium from a theoretical point of view the conditions for the investigation of acidic properties should possess a particular simplicity.[17]

At first ordinary benzene "zur Analyse" was used and a few experiments carried out with solutions of benzoic acid, acetic acid and phenol, but the results were rather inconsistent.   With benzene alone there was a certain amount of reaction, due no doubt to the small amount of water contained in it.

The individual experiments showed that the linear relation between $\sqrt{x}$ and time was valid although the drift noticed in some of the aqueous solutions set in earlier in the benzene solutions.

Experiments with *dry* benzene alone showed that there was no reaction which gave rise to an evolution of gas although small amounts of grayish-black powder were produced.   This was shown to be finely divided mercury.

[16] Zecchini, *Gazz. chim. ital.*, 27, I, 466 (1897).

[17] *Cf.* Brönsted, *Z. angew. Chem.*, 43, 229 (1930).

Then measurements were made with a series of solutions of phenol in *dry* benzene. These experiments showed that just as in aqueous solution there is a linear relation between reaction velocity and phenol concentration. The data are given in Table IX, where the first column indicates the volume molality of the acid; k is calculated as in the experiments with aqueous solutions.

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TABLE IX

EXPERIMENTS IN BENZENE SOLUTION

</div>

Molality of phenol	0.0	0.05	0.10	0.20	0.30	0.40	0.50
$k \cdot 10^2$	0.0	0.53	1.16	2.16	3.30	4.46	5.66

It should be noted that, as might be expected, the line connecting velocity constant and phenol concentration passes through the origin on extrapolation, while in aqueous solution this is not the case.

The reaction with benzoic acid dissolved in dry benzene is curious in that the linear relation (10) does not hold good. It was not possible therefore to derive a velocity constant from these experiments.

Discussion

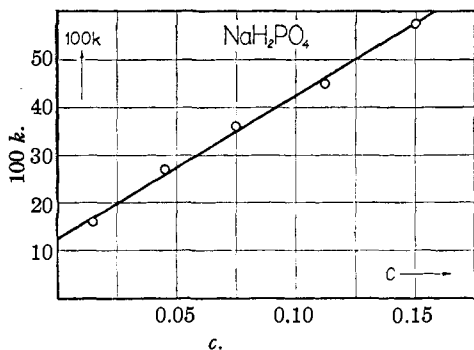From the standpoint of the present theory one would anticipate that the dissolution of sodium from the amalgam in a buffer solution in an acid medium of high dielectric constant like water could be represented as a composite effect of several reactions, each being determined by the concentrations of the different acids present and their individual reaction constants. Thus plotting the velocity constant of the experiments with a certain buffer against its concentration at constant hydrogen-ion concentration, eliminating possible salt effects, a straight line should appear, the slope of which determines the particular reaction constant of the acid buffer component. The intercept of this line with the ordinate axis at zero concentration of buffer should give the combined effect of the hydrogen ion and the solvent. By changing the buffer ratio the two last mentioned effects might be separated.

Fig. 2.—Sodium dihydrogen phosphate.

When considering the experiments with phosphate, glycocoll and phenol buffers, the results are actually very well represented by a straight line, with different slope in the three cases.

This is shown by Figs. 2–4, where the velocity constant 100 k is plotted

against the molality of acid constituent of the buffer. From the figures the molal velocity constants k_1 defined as

$$k_1 = \frac{k}{c_A}$$

where c_A is the molality of acid, and determined by the slope of the straight lines are calculated for the three acids and given in Table X. This also contains the k-values of the secondary phosphate ion calculated from the
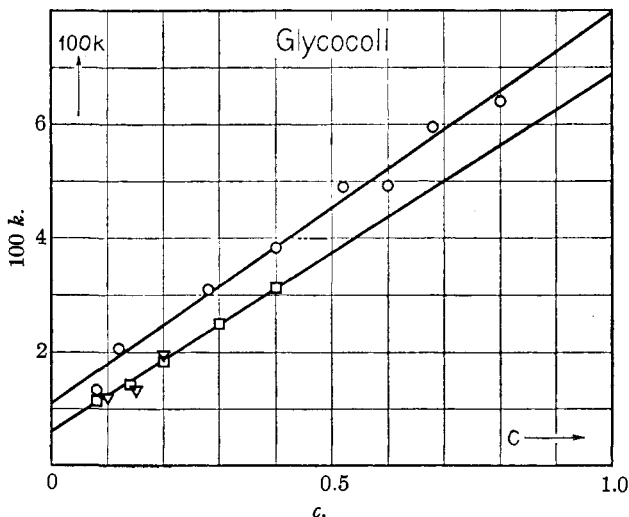

Fig. 3.—○, "$9/_1$ Glycocoll"; □, "$7/_3$ glycocoll";
△, "$6/_4$ glycocoll."

figures in Table I, the total effect being attributed to this ion. The strength constants[18] of the four acids are also given in the table.

TABLE X

MOLAL VELOCITY CONSTANT

	Acid	100 k_1	K
1	$H_2PO_4^-$	290	$10^{-7.2}$
2	Glycocoll$^\pm$	6.5	$10^{-9.9}$
3	Phenol	0.46	10^{-10}
4	HPO_4^{--}	2.6	$10^{-12.4}$

The results obtained with the first three of these acids, where the reaction velocity was found to vary linearly with the acid concentration at constant hydrogen-ion concentration, are strongly confirmatory of the view that the dissolution is due to a reaction between the amalgam and the acid molecule considered. As shown by the figures in Table X there also seems to be a tendency for k_1 to increase with K. This tendency, however, is somewhat

[18] Cf. Bjerrum and Unmack, Kgl. Danske Videnskab. Selskab Biol. Medd., 9, 1 (1919).

obscured by a simultaneous effect of the charge type of the acid. This effect may be the reason why phenol and glycocoll act so differently although they are almost identical as regards acid strength. If, as proposed in the introduction, the primary reaction consists in a union of the acid molecule with an electron, the positive charge of the acid group in the glycocoll would increase the velocity. On the other hand, the secondary phosphate ion reacts relatively rapidly in spite of its double negative charge. As a possible e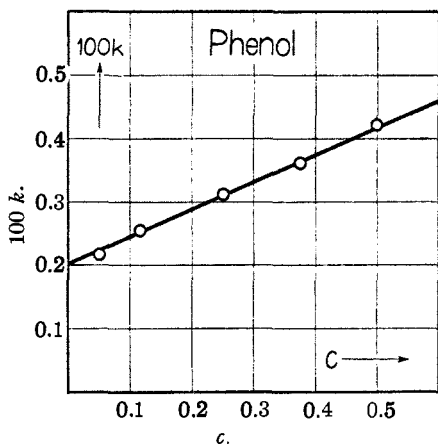xplanation of this result one may assume an electrostatic reaction between the acid and the sodium ion of the amalgam as suggested above to be the primary mechanism in certain cases. The double charge and high concentration of the HPO_4-ion applied should be favorable to such a course of reaction. For a definite conclusion as regards the influence of the strength and charge type of the different acids the material, however, does not suffice.

The extrapolated values of the velocity constant at zero concentration of the buffer are markedly higher in solutions of high acidity. This is what could be expected when those values are taken to represent the combined effect of hydrogen ion and solvent. For the five buffers in question the figures are as given in Table XI.

Fig. 4.—Phenol, benzene solution.

TABLE XI

VELOCITY CONSTANT AT ZERO BUFFER CONCENTRATION

Buffer	A/B	c_{H^+}	$100\ k_0$
Phosphate	0.4	$260 \cdot 10^{-10}$	11
Glycocoll	8.0	$10 \cdot 10^{-10}$	1.2
Glycocoll	1.3	$1.6 \cdot 10^{-10}$	0.6
Glycocoll	0.5	$0.6 \cdot 10^{-10}$	.6
Phenol	2.0	$2 \cdot 10^{-10}$	.2

A/B is the ratio of acid to base in the buffer; k_0 represents the value of k extrapolated to zero concentration. The experiments with the phosphate and the most acid glycocoll buffer lead to a value of the order 10^7 for the catalytic constant k_H of the hydrogen ion. The experiments at lower acidity are, however, not very well compatible with that value. It seems therefore not possible from the above experiments to determine more than the order of magnitude of the constant for the hydrogen ion.

If we take the above value $k_H = 10^7$ as approximately true, then from equation (13) the reaction time of normal hydrochloric acid with sodium amalgam of a concentration as used in these experiments is calculated as

$$t_\infty = \frac{3.5}{k_H} \text{ min.} = 2 \cdot 10^{-5} \text{ sec.}$$

The extremely high reaction rate of the hydrogen ion H_3O^+ conforms with its high strength as an acid. It follows from the value of t_∞ that in such acid solutions the above equations are no longer applicable, and that the rate of reaction is here determined entirely by the diffusion process of the reacting substances into the surface of interaction.

The slightness of the influence of the acid concentration found by Fraenckel and Heinz when strong acids as hydrochloric are employed is in conformity with the conclusion as to the nature of this reaction.

In Fig. 5 the data of Table IX comprising the results with phenol in benzene solution are represented. It is clearly shown by this graph that the velocity is directly proportional to the concentration of the

Fig. 5.—Phenol, aqueous buffer solution.

acid. These results therefore are in full conformity with the theory set forth for the interaction between metals and acids.

It is interesting to note that the reaction constant of phenol in benzene is more than twenty times its value in aqueous solution.

Summary

1.   The dissolution of a pure metal in an acid solution is most probably the result of a chemical reaction between an electron in the metal and a molecule of the acid. This idea conforms with the extended theory of acids and bases.

2.   Sodium as amalgam dissolves in solutions of various acids with a velocity which is directly proportional to the square root of the sodium concentration. For such a case the time required for the reaction to be completed is finite.

3.   The reaction of sodium amalgam with aqueous sodium hydroxide solutions is slow, but does not give reproducible results.

4.   In a number of experiments with aqueous phosphate, glycocoll and phenol buffers of constant hydrogen-ion concentration, the velocity showed a linear increase with increasing buffer concentration. This is interpreted
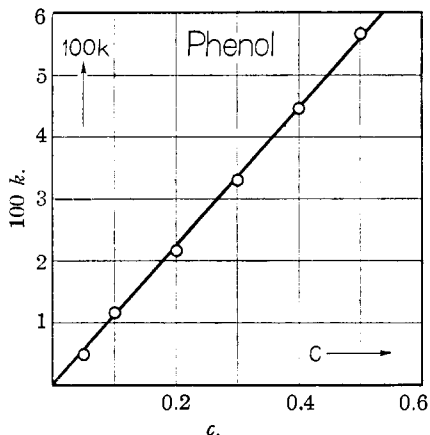
as a proof of the correctness of the idea that dissolution of sodium is due to the reaction of the metal (electron) with the acid molecule.

5.   The molal reactivity constant of various acids shows a tendency to increase with the strength of the acid.   The effect of the charge of the acid and other effects, however, may partly mask the strength effect.

6.   The roseo cobaltic ion which bears three positive charges reacts very rapidly with sodium amalgam.   This is explained as being due to its high positive charge and the resulting strong attraction to the electron.

7.   Corresponding to the high strength of the hydrogen ion H_3O^+ this acid reacts with extreme speed.   The dissolution of sodium amalgam in strong acids is therefore governed chiefly by the rate of the diffusion process.

8.   The rate of reaction of sodium amalgam with a solution of phenol in dry benzene is proportional to the phenol concentration.

COPENHAGEN, DENMARK

THERMAL ENERGY STUDIES.   I.   PHENYL DERIVATIVES OF METHANE, ETHANE AND SOME RELATED COMPOUNDS[1]

BY RICHARD H. SMITH AND DONALD H. ANDREWS

The importance of energy as a factor in chemistry has been recognized for a great many years and it has been a source of inspiration in many fields of research from the time of Thomsen and Berthelot down to the present day.   Broadly speaking, if we knew the energy relationships of the molecule completely enough, we would be able to predict all the modes of chemical behavior.

One must admit, however, that it is very difficult to do chemical thinking in terms of energy on the basis of our present knowledge.   Although we intuitively connect chemical behavior with structural formulas or the position of an element in the periodic table, we have never been able to draw a sufficiently intimate picture of the relation of energy to molecular and atomic structure, so that we can feel instinctively the role of energy in determining the course of a reaction, particularly when it involves complex molecules.   What we need is a much more detailed knowledge of the energy associated with the different parts of the molecule and how it varies with temperature, environment and distortion or excitation of the molecule itself.

For answering these questions, one of the most valuable types of information is heat capacity data especially over a wide range of temperature. During the past fifteen years there has been a great deal of work done in

[1] From the dissertation submitted by R. H. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy.